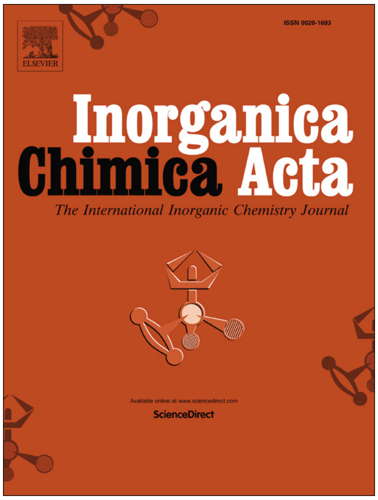

Research paper

Synthesis, structure and properties of nickel and copper complexes containing N,O-hydrazone Schiff base ligand

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Synthesis, structure and properties of nickel and copper complexes containing N,O-hydrazone Schiff base ligand

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Keywords: copper; nickel; oxidation; catalysis; Schiff base; DFT

Dedicated to Prof. Carlo Mealli, in recognition of his contribution to the understanding of Chemistry.

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ABSTRACT

The compound 2-(1-(2-methyl-2-phenylhydrazono)ethyl)phenol, HL^{NNMePh}, was synthesized by solvent-free condensation of *o*-hydroxyacetophenone and *N*,*N*-methylphenylhydrazine and was analytically and spectroscopically characterized. The reaction of HL^{NNMePh} with nickel acetate and copper acetate in the presence of NEt_3 resulted the corresponding $[M(L^{NNMePh})_2]$ complexes (M = Ni, **1**; Cu, **2**), which were structurally characterized by X-ray diffraction methods. A four-coordinate square planar environment around the metal centre was found for both compounds, in which the two L^{NNMePh} ligands act as bidentate N,O-chelators and exhibit a pseudo-*trans* conformation. These compounds are the first structurally characterized transition metal complexes containing the κ^2-*N*,*O*-2-(1-(2-methyl-2-phenylhydrazono)ethyl)phenolate ligand, L^{NNMePh}. Copper complex $[Cu(L^{NNMePh})_2]$, **2**, was tested as catalyst, in combination with TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl radical), for the aerobic oxidation of benzyl alcohol, as model reaction. Low yields of the corresponding aldehyde were observed by using air at atmospheric pressure as the oxidant in toluene as solvent.

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1. Introduction

Oxidation catalysis is a topic of permanent interest and therefore the development of new catalytic systems, based on transition metal compounds and using green oxidants, is an active research area [1]. In particular, alcohol oxidation is an essential transformation for which sustainable processes are continually sought [2]. Oxidation by air or molecular oxygen represents the cleanest, most sustainable option and the catalyst activity of several transition metals in this transformation is well established [3]. In particular, since the Semmelhack report [4], the efficiency of copper compounds, with the TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl radical) co-catalyst, in the selective aerobic alcohol oxidations is unquestionably. Many highly efficient copper catalysts have been developed [5,6,7,8,9], with new ligands [10,11,12,13], new TEMPO variants [14], or new reaction conditions [15,16,17,18,19].

In continuation of our interest in exploring Cu/TEMPO-catalyzed aerobic oxidation of alcohols [20], we looked for novel bidentate N,O-ligands for the preparation of new copper catalyst precursors. Herein, we describe the synthesis, structure and DFT calculations of compounds $[M(L^{NNMePh})_2]$ (M = Ni, **1**; Cu, **2**) containing the κ^2-*N*,*O*-2-(1-(2-methyl-2-phenylhydrazono)ethyl)phenolate ligand, L^{NNMePh}. These compounds are the first structurally characterized transition metal complexes containing this ligand, according to a CSD search [21]. Copper complex $[Cu(L^{NNMePh})_2]$, **2**, was tested as catalyst, in combination with TEMPO, for the aerobic oxidation of benzyl alcohol, as model reaction. In contrast with other related systems previously reported by us [20], only low yields of the corresponding aldehyde were observed by using air at atmospheric pressure as the oxidant.

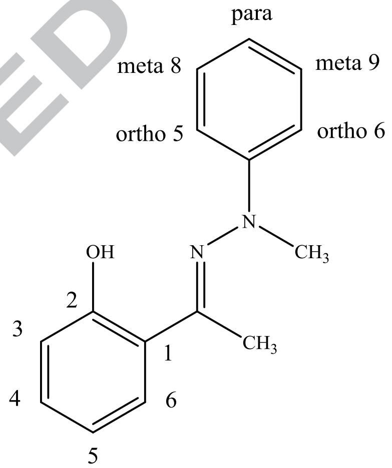
2. Experimental section

2.1. General

All preparations and other operations were carried out under aerobic conditions. Solvents were purified and dried appropriately prior to use, using standard procedures. Chemicals were obtained from commercial sources and used as supplied. Infrared spectra were recorded on a Perkin-Elmer Spectrum Two spectrophotometer (pressed KBr pellets). NMR spectra were recorded at the Centro de Investigaciones, Tecnología e Innovación (CITIUS) of the University of Sevilla by using Bruker models Avance III 300 MHz spectrometer. $^{13}C\{^1H\}$ and ^1H shifts referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from $Si(CH_3)_4$. Magnetic moment was measured in the solid state, at room temperature, with a Sherwood Scientific (Cambridge Research Laboratory) magnetic balance. The gas chromatograms (GC) were obtained using a Varian Chromatogram CP-3800 with nitrogen as the carrier gas. The chromatogram used a Varian automatic injector, model CP-8410, flame ionisation detector (FID), and a Varian column, model CP-8741. Elemental microanalyses (C, H, N) were carried out on an Elemental LECO CHNS 93 analyzer by the Microanalytical Service of the University of Sevilla (CITIUS).

2.2. Synthesis of 2-(1-(2-methyl-2-phenylhydrazono)ethyl)phenol, HL^{NNMePh}

1-Methyl-1-phenylhydrazine (0.6 ml, 5 mmol) and a catalytic amount of *p*-toluenesulfonic acid (5 mg, 0.03 mmol) were added to *o*-hydroxyacetophenone (0.62 mL, 5 mmol). The mixture was left to react for 24 h at room temperature and then was purified by chromatography (SiO_2, toluene as eluent). The extract was dried with Na_2SO_4. After removal of the solvent under low pressure, the hydrazone HL^{NNMePh} was obtained as a yellow crystalline solid (340 mg, 1.5 mmol, 30 % yield). IR (KBr, υ, cm^{-1}): 3418, 3059, 2877, 2807, 1944, 1640, 1599, 1492, 1448, 1364, 1303, 1251, 1221, 1158, 1097, 1029, 996, 961, 837, 751, 692, 648, 620, 561, 520, 437. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.45 (s, 3H, NC-C*H*$_3$), 3.21 (s, 3H, NN-C*H*$_3$), 6.89 (d, 1H, H-5), 6.95 (m, 1H, H$_{para}$), 6.98 (m, 2H, H$_{ortho}$), 7.03 (dd, *J* = 1.5, 7.6 Hz, 1H, H-4), 7.26 (m, 2H, H$_{meta}$), 7.37 (dd, *J* = 1.5, 7.2 Hz, 1H, H-3), 7.56 (dd, *J* = 1.5, 7.9 Hz, 1H, H-6), 13.5 (br s, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 15.37 (NC-*C*H$_3$), 43.64 (NN-*C*H$_3$), 115.7 (C$_{para}$), 118.0 (C-4), 118.9 (C-5), 119,0 (C-1), 121.1 (C$_{ortho}$), 128.8 (C-6), 129.1 (C$_{meta}$), 132 (C-3), 150.5 (C$_{ipso}$), 160.5 (C-2), 171.9 (C=N). For the notation of ^{1}H and ^{13}C signals, based on heteronuclear and long range heteronuclear correlations, see the scheme:



*2.3. Synthesis of [M(L^{NNMePh})$_2$] (M = Ni, **1**; Cu, **2**) complexes*

To a solution of HL^{NNMePh} (0.24 g, 1 mmol) in MeOH (25 ml) was added Et_3N (0.14 mL, 1 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (0.13 g, 0.5 mmol). The resulting solution was stirred at room temperature until the compound [Ni(L^{NNMePh})$_2$] **1** precipitated. The brown solid was filtered, washed with diethyl ether and dried (0.19 g, 72 % yield). X-ray quality single crystals of **1** were obtained by crystallization from CH_2Cl_2. IR (KBr, υ, cm^{-1}): 3417, 3061, 3029, 2925, 2813, 1923, 1637, 1597, 1560, 1499, 1438, 1349, 1328, 1257, 1247, 1134, 1109, 1033, 999, 942, 875, 846, 756, 743, 691, 624, 587, 533, 452. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.27 (s, 3H, NC-C*H*$_3$), 3.57 (s, 3H, NN-C*H*$_3$), 5.75 (t, *J* = 7.2 Hz, 1H, H-6), 6.43 (t, *J* = 7.5 Hz, 1H, H-4), 6.87 (m, 2H, H_{para} + H-5), 7.12 (d, *J* = 7.8 Hz, 1H, H_{ortho5}), 7.27 (m, 2H, H-3 + H_{ortho6}), 7.38 (m, 2H, H_{meta}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75MHz): δ 18.8 (NC-*C*H$_3$), 42.2 (NN-*C*H$_3$), 111.9 (C_{ortho5}), 112.2 (C_{ortho6}), 115.1 (C-4), 117.9 (C_{para}), 118.2 (C-1), 120.9 (C-6), 129.6 (C_{meta}), 130.2 (C-3), 133.0 (C-5), 149.8 (C_{ipso}), 164.9 (C-2), 173.9 (C=N). Elemental Anal. Calc. for $C_{30}H_{30}NiN_4O_2$: C, 67.06; H, 5.63; N 10.92. Found: C, 66.19; H, 5.57; N, 10.28 %.

Following a similar synthetic procedure as described for **1** but using $Cu(AcO)_2 \cdot H_2O$ (0.10 g, 0.5 mmol) as reagent, the compound $[Cu(L^{NNMePh})_2]$ **2** was obtained as red crystals (0.22 g, 81% yield). X-ray quality single crystals of **2** were obtained by crystallization from CH_2Cl_2. IR (KBr, υ, cm^{-1}): 3417, 3062, 3017, 2888, 1833, 1637, 1599, 1560, 1522, 1498, 1440, 1350, 1237, 1129, 1110, 932, 868, 754, 693, 573, 525, 442. μ_{eff} = 1.61 μ_B at 298 K. Elemental Anal. Calc. for $C_{30}H_{30}CuN_4O_2$: C, 66.46; H, 5.58; N 10.33. Found: C, 65.36; H, 5.55; N, 10.22 %.

2.4. General procedure for aerobic catalytic oxidation of benzyl alcohol

Reactions performed at atmospheric pressure were conducted in a 50 ml round bottom flask or in vials of 20 ml capacity, at the desired temperature. The catalyst (0.025 mmol) and TEMPO (0.05 mmol) were first charged to the flask and the toluene (2 mL) and the benzyl alcohol (1.0 mmol) were then added and the mixture was stirred for the duration of the reaction. When the reaction had finished, the reaction mixture was filtered, added an internal standard (50 μl of dodecane) and diethyl ether up to 10 mL. The homogenized mixture was analyzed by gas chromatography. At least, two determinations were carried out for each catalytic essay.

2.5. X-ray structural studies

A summary of the crystallographic data and structure refinement results for $[M(L^{NNMePh})_2]$ (M = Ni, **1**; Cu, **2**) compounds is given in Table S1 (Supplementary material). Crystals of these new compounds coated with dry perfluoropolyether were mounted on a glass fiber and fixed under a cold nitrogen stream. The intensity data were collected on a Bruker-Nonius X8ApexII CCD area detector diffractometer using Mo-$K\alpha$ radiation source (λ = 0.71073 Å) fitted with a graphite monochromator. The data collection strategy used was ω and ϕ rotations with narrow frames (width of 0.50 degree). Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times and no decay was observed. The data were reduced using SAINT [22] and corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied (SADABS) [23]. The structures were solved by direct methods using SIR-2002 [24a] and refined against all F^2 data by full-matrix least-squares techniques using SHELXL-2016/6 [24b] minimizing $w[Fo^2-Fc^2]^2$. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of compounds **1** and **2** were included from calculated positions and allowed to ride on the attached atoms with isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) those U_{eq} values of the corresponding attached atoms.

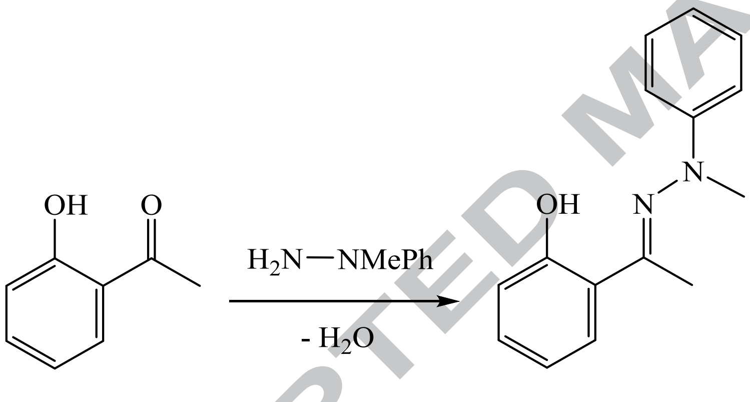
2.6. Computational details

The electronic structure and geometries of the $[M(L^{NNMePh})_2]$ (M = Ni, Cu) compounds were computed using density functional theory at the B3LYP level [25] and the 6-31G(d,p) basis set was used for all the atoms. The optimized geometries of all the compounds were characterized as energy minima by the nonexistence of imaginary frequencies (NImag = 0) in the diagonalisation of the analytically computed Hessian (vibrational frequencies calculations). The DFT calculations were performed using the Gaussian 09 suite of programs [26]. Cartesian coordinates and energies of all optimized compounds are collected in Tables S3 and S4 (Supplementary Material).

3. Results and discussion

*3.1. Synthesis and molecular structure of complexes $[M(L^{NNMePh})_2]$ (M = Ni, **1**; Cu, **2**)*

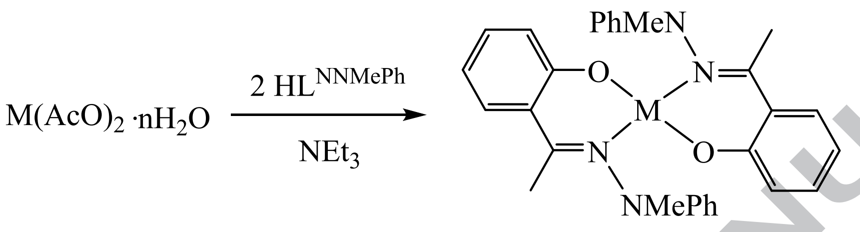
The precursor ligand HL^{NNMePh} was prepared by condensation of *o*-hydroxyacetophenone and *N*,*N*-methylphenylhydrazine in the absence of solvent (Scheme 1) and it was isolated as a yellow solid in medium yields. A brief mention to the synthesis of this compound has previously appeared [27]. Analytical and spectroscopic data were in agreement with the proposed formulation. The IR spectrum showed an intense absorption centered at around 1640 cm^{-1} that was attributed to the C=N stretching vibration. The ^{1}H NMR spectrum showed the methyl resonances of the ketimine, N=C-*Me*, and the hydrazine, N-N-*Me*, as a singlets at 2.45 and 3.21 ppm, respectively, while the O-H proton appeared close to 14 ppm. This high downfield signal shift suggested the presence of an intramolecular hydrogen bond with the nitrogen atom, as described in other related systems [20a,b,28]. The imino carbon atom *C*=N resonates at around 172 ppm in the ^{13}C{^{1}H} NMR spectrum, while the aromatic C-H bonds showed the typical pattern in both ^{1}H and ^{13}C{^{1}H} NMR spectra.



HL^{NNMePh}

Scheme 1

The reaction of the ligand precursor HL^{NNMePh} with nickel acetate and copper acetate in the presence of NEt_3 afforded the corresponding complexes [M(L^{NNMePh})$_2$] (M = Ni, **1**; Cu, **2**) in good yields (Scheme 2). They were obtained as brown (M = Ni) and red (M = Cu) crystalline solids. Evidence of coordination of the L^{NNMePh} ligand came from the IR spectra in which the C=N stretching vibration is slightly shifted to lower wavenumber than that found in the HL^{NNMePh} compound (1637 cm^{-1} for **1** and **2**, respectively, with respect to 1640 cm^{-1} found in HL^{NNMePh}). [Ni(L^{NNMePh})$_2$] was diamagnetic and a fully assignation of ^{1}H and ^{13}C resonances was achieved with the help of 2D NMR experiments (HSQC and HMBC). Assignations are reported in the experimental section. The most noteworthy NMR feature is the observation of two different signals in the ^{1}H NMR spectrum, at 7.12 and 7.27 ppm, for the ortho C-H hydrogen atoms of the phenyl group joined to nitrogen, indicating that the rotation of the phenyl group around the C-N bond is blocked. The corresponding signals of the ortho carbons appear at 111.9 and 112.2 ppm in the ^{13}C{^{1}H} NMR spectrum (see Fig. S1 at the supplementary material). Compound [Cu(L^{NNMePh})$_2$] was paramagnetic with an effective magnetic moment of 1.61 μ_B at 298 K, which was in agreement with the square-planar geometry of this complex (see below).



M = Ni, **1**; Cu, **2**

Scheme 2

Complexes [M(L^{NNMePh})$_2$] (M = Ni, **1**; Cu, **2**) were structurally characterized by X-ray crystallography. Their molecular structures are shown in Fig. 1, while selected bond distances and angles are given in Tables 1 and 2 for **1** and **2**, respectively. Both compounds show a four-coordinate square planar environment around the metal centre, which is distorted for the copper complex. In fact, the τ_4 parameters [29] for **1** and **2** are 0 and 0.33º, respectively, while the related τ_4' parameters [30] are 0 and 0.31º. The two L^{NNMePh} ligands act as bidentate *N*,*O*-chelators and lie in a pseudo-*trans* conformation. Each L^{NNMePh} ligand creates with the metal a six-membered metallacycle, which is close to the planarity for **2**, but slightly folded for **1**. These conformations have been identified in related complexes as planar and step configurations, respectively (see Fig. S2, Supplementary material) [31]. The dihedral angle between the two coordination planes O-Ni-N is 0º for complex **1**, in agreement with analogous structurally related Ni-derivatives [32]. By contrast, the same angle for **2** is 32.4º, in harmony with other structurally related Cu-complexes [33]. As expected, the Ni-O1 and Ni-N1 bond lengths of 1.823(2) and 1.926(2) Å, respectively, are slightly shorter than Cu-O1 and Cu-N1 ones (1.8681(11) and 2.0017(14) Å, respectively). The relative orientation of the phenyl groups in both complexes is dissimilar, showing complex **1** an *up-down* conformation, while for **2** is *up-up* (Fig. S2).

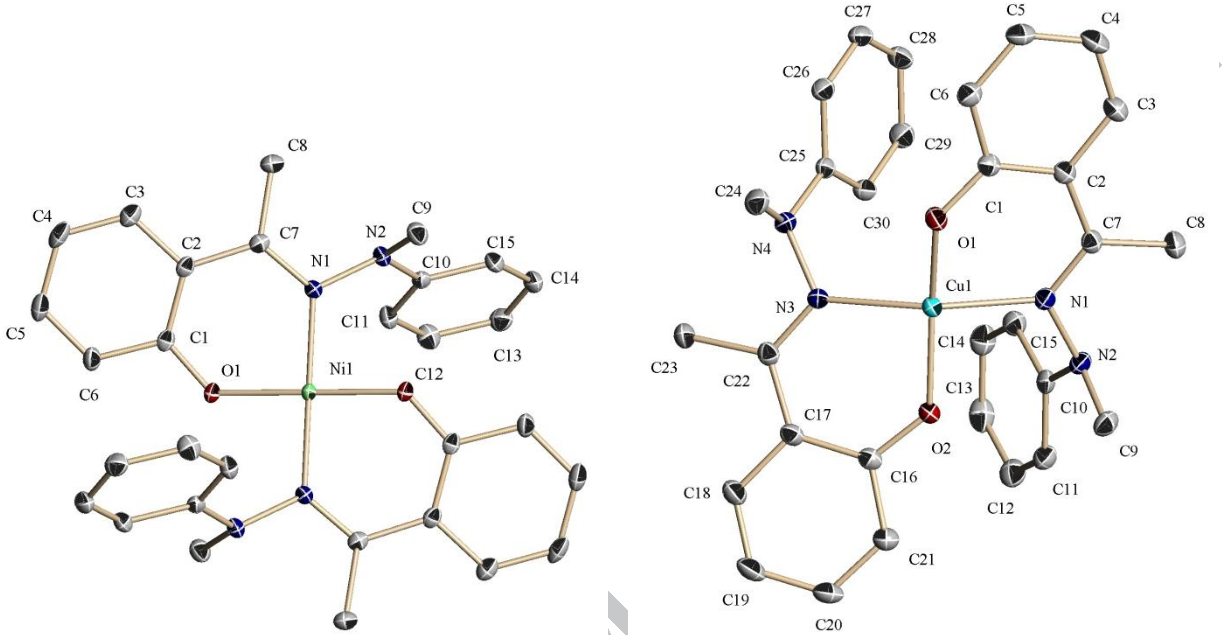


Fig. 1 Molecular structures of complexes $[M(L^{NNMePh})_2]$ (M = Ni, **1**, left; Cu, **2**, right).

3.2 DFT analysis of $[M(L^{NNMePh})_2]$ complexes (M = Ni, Cu)

DFT calculations were carried out at the B3LYP level of theory for $[M(L^{NNMePh})_2]$ complexes (M = Ni, Cu) and Fig. 2 and S3 shows their optimized structures. The combination of the selected method and basis sets provided a good structural description of both complexes; according to the comparison of the structural parameters of the optimized geometries with those of the crystal structures (see Table S2, Supplementary Material). In order to gain additional information concerning the dissimilar phenyl conformations observed in the experimental molecular structures, the conformers the *up-up* for nickel and *up-down* for copper were also computed. The optimized resulting structures are shown in Fig. S4 (Supplementary Material). The calculated energy difference between the two conformations is less than 1 kcal·mol^{-1} for both nickel and copper complexes (see Table S4) and consequently the adoption of one conformer over the other is simply due by crystal-packing forces.

Table 1

Selected bond lengths (Å) and angles (°) for $[Ni(L^{NNMePh})_2]$ complex, **1**.

Ni(1)-O(1)	1.823(2)	N(1)#1-Ni(1)-N(1)	180.0
Ni(1)-N(1)	1.926(2)	C(7)-N(1)-N(2)	113.7(2)
O(1)-C(1)	1.307(4)	C(7)-N(1)-Ni(1)	127.3(2)
N(1)-N(2)	1.423(3)	N(2)-N(1)-Ni(1)	118.95(18)
N(1)-C(7)	1.313(4)	C(10)-N(2)-N(1)	116.8(2)
O(1)-Ni(1)-N(1)	91.29(10)	C(10)-N(2)-C(9)	121.1(3)
O(1)-Ni(1)-O(1)#1	180.0	N(1)-N(2)-C(9)	113.9(2)
O(1)-Ni(1)-N(1)#1	88.71(10)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z.

Table 2

Selected bond lengths (Å) and angles (°) for $[Cu(L^{NNMePh})_2]$ complex, **2**.

Cu(1)-O(1)	1.8681(11)	O(1)-Cu(1)-N(1)	91.02(5)
Cu(1)-O(2)	1.8660(12)	N(3)-Cu(1)-N(1)	158.85(6)
Cu(1)-N(1)	2.0017(14)	C(7)-N(1)-N(2)	114.66(14)
Cu(1)-N(3)	2.0013(15)	C(7)-N(1)-Cu(1)	128.33(12)
O(1)-C(1)	1.305(2)	N(2)-N(1)-Cu(1)	116.99(10)
O(2)-C(16)	1.305(2)	C(10)-N(2)-N(1)	114.09(13)
N(1)-N(2)	1.4355(19)	C(10)-N(2)-C(9)	120.73(14)
N(1)-C(7)	1.305(2)	N(1)-N(2)-C(9)	113.05(14)
N(3)-N(4)	1.433(2)	C(22)-N(3)-N(4)	114.70(14)
N(3)-C(22)	1.304(2)	C(22)-N(3)-Cu(1)	128.50(12)
O(2)-Cu(1)-O(1)	155.29(6)	N(4)-N(3)-Cu(1)	116.80(10)
O(2)-Cu(1)-N(3)	91.17(6)	C(25)-N(4)-N(3)	114.09(13)
O(1)-Cu(1)-N(3)	93.59(5)	C(25)-N(4)-C(24)	119.62(14)
O(2)-Cu(1)-N(1)	93.22(6)	N(3)-N(4)-C(24)	112.92(13)

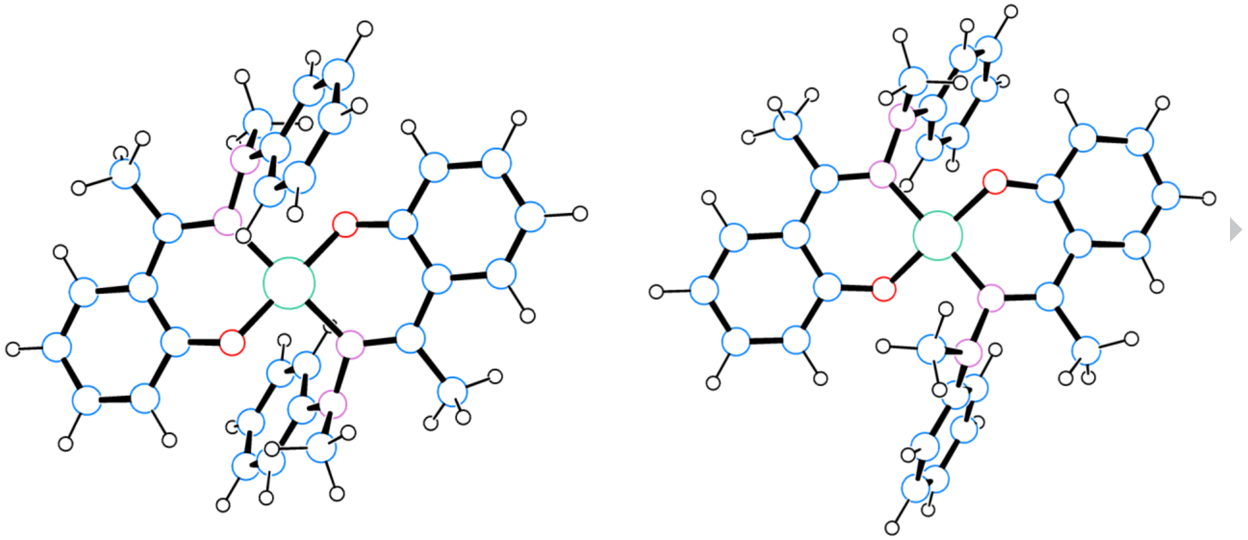
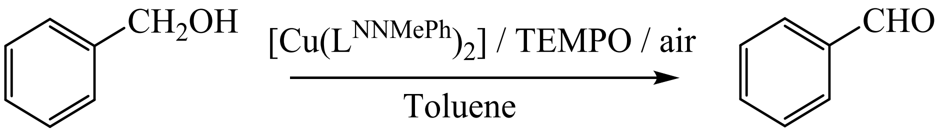


Fig. 2 Optimized structures of [M(L^{NNMePh})$_2$] complexes (M = Ni, left; Cu, right).

3.3 Benzyl alcohol oxidation catalyzed by complex [Cu(L^{NNMePh})$_2$] ***2***

We recently described the good catalytic activity of compound [Cu(L^{allyl})$_2$] (L^{allyl} = *N*-allyl-*o*-hydroxyacetophenoniminato) in the TEMPO co-catalyzed aerobic oxidation of alcohols with air at atmospheric pressure and room temperature [20a]. The similarity of [Cu(L^{NNMePh})$_2$] **2** with the latter complex prompted to us to investigate the activity of **2** in the same oxidation reaction. The benzyl alcohol and toluene were selected as the appropriate alcohol substrate and solvent, respectively, for preliminary assays under the same reaction conditions previously optimized for [Cu(L^{allyl})$_2$] (Scheme 3). Reactions were carried out on the 1 mmol scale in the presence of a catalytic amount of the copper complex and TEMPO in 2 mL of solvent. The optimum ratio of [Cu]:TEMPO was demonstrated to be 1:2 in previous related systems [20]; therefore, the ratio 1:0.05:0.025 for alcohol:TEMPO:catalyst was selected as optimal in order to perform the catalytic essays.



Scheme 3

Preliminary results are shown in Table 3 with those known for complex [Cu(L^{allyl})$_2$] for an appropriate comparison. Firstly, control experiments without complex **2** and without TEMPO produced practically no detectable conversion (entries 1 and 2, respectively), establishing that the presence of both the copper catalyst and TEMPO as co-catalyst was essential for oxidation to take place. After 18 h at room temperature the conversion and the yield are low (both in acetonitrile, entry 3, as in toluene, entry 4) and this situation contrast with that previously observed for [Cu(L^{allyl})$_2$] (entry 5). Better results were also obtained previously by us for the Cu/TEMPO-catalyzed oxidation carried out in scCO$_2$ or in toluene with other related systems [20b,c]. By increasing the temperature to 60 ºC the results do not improve (entry 6) being worse than those reported for [Cu(L^{allyl})$_2$] (entry 7).

Table 3 Oxidation of the benzyl alcohol with air catalyzed by copper complexes in the presence of TEMPO.[a]

Entry	Catalyst	Time (h)	Temperature (^{0}C)	Yield(%)
1	-	18	25	0
2	[Cu(L^{NNMePh})$_2$] **2** [b]	18	25	2
3	[Cu(L^{NNMePh})$_2$] **2** [c]	18	25	8
4	[Cu(L^{NNMePh})$_2$] **2**	18	25	10
5	[Cu(L^{allyl})$_2$] [d]	18	25	84 [d]
6	[Cu(L^{NNMePh})$_2$] **2**	6	60	14
7	[Cu(L^{allyl})$_2$] [d]	6	60	84 [d]

[a] Reaction conditions: 0.025 mmol of copper complex, 0.05 mmol of TEMPO, 1 mmol of benzyl alcohol, 2 mL of toluene. Air at atmospheric pressure. After work-up, yields were determined by GC. [b] Without TEMPO. [c] With acetonitrile as solvent. [d] See reference 20a.

4. Conclusions

The precursor ligand HL^{NNMePh} and the corresponding complexes [M(L^{NNMePh})$_2$] (M = Ni, **1**; Cu, **2**) have been synthesized and spectroscopically characterized. [M(L^{NNMePh})$_2$] complexes have also been structurally characterized and they exhibit a four-coordinate environment around the metal centre, where the two L^{NNMePh} ligands act as bidentate N,O-chelators and exhibit a pseudo-*trans* conformation. Copper complex [Cu(L^{NNMePh})$_2$], **2**, was tested as catalyst, in combination with TEMPO, for the aerobic oxidation of benzyl alcohol, as model reaction. Surprisingly, using air at atmospheric pressure as the oxidant only low yields of the corresponding aldehyde were observed in toluene as solvent. These results are in contradiction with those observed for other related systems previously described by us [20].

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Appendix A. Supplementary material

CCDC 1531575 (**1**) and 1531576 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data for [M(L^{NNMePh})$_2$] (M = Ni, **1**; Cu, **2**) complexes, comparison of computed and experimental selected structural parameters of compounds **1** and **2**, and structures, coordinates and energies of the optimized compounds are available. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/...

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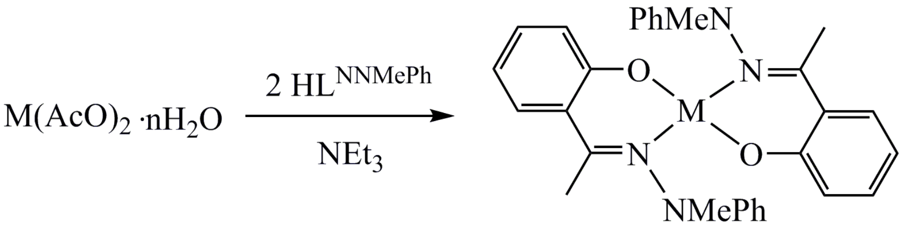
SYNOPSIS

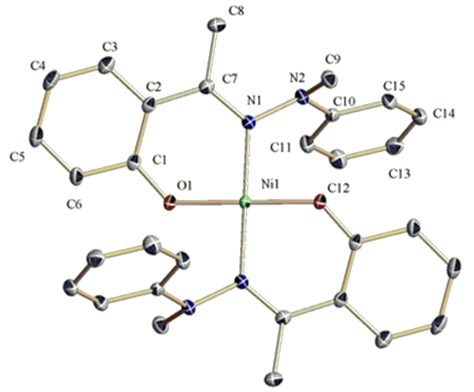
Synthesis, structure and properties of nickel and copper complexes containing N,O-hydrazone Schiff base ligand

María del Mar Conejo,*[a] Jorge Cantero,[a] Antonio Pastor,*[a] Eleuterio Álvarez,[b] and Agustín Galindo[a]

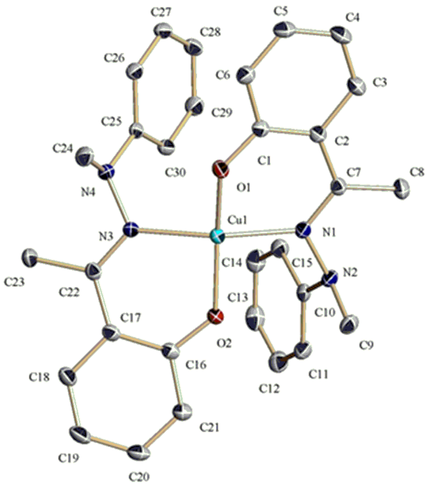
Complexes $[M(L^{NNMePh})_2]$ (M = Ni, **1**; Cu, **2**) were synthesized and characterized. These compounds are the first structurally characterized transition metal complexes containing the κ^2-*N*,*O*-2-(1-(2-methyl-2-phenylhydrazono)ethyl)phenolate ligand, L^{NNMePh}.



M = Ni, **1**



M = Cu, **2**



HIGHLIGHTS

Synthesis, structure and properties of nickel and copper complexes containing N,O-hydrazone Schiff base ligand

María del Mar Conejo,* [a] Jorge Cantero,[a] Antonio Pastor,* [a] Eleuterio Álvarez,[b] and Agustín Galindo[a]

- The compound HL^{NNMePh} are prepared by a solvent-free synthetic procedure.
- Complexes $[M(L^{NNMePh})_2]$ (M = Ni, **1**; Cu, **2**) are synthesized and characterized.
- The first structurally characterized complexes with the L^{NNMePh} ligand are reported.